

Generate Models for Release of Radionuclides and Neutron Absorbers from Titanate Ceramic Waste Forms

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Activity Plan

GENERATE MODELS FOR RELEASE OF RADIONUCLIDES AND NEUTRON ABSORBERS FROM TITANATE CERAMIC WASTE FORMS

for

Plutonium Immobilization Project

Lawrence Livermore National Laboratory

Revision 0
July 31, 1998.

APPROVALS:

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1. Purpose and Scope

One of the waste forms being considered for the permanent disposal of excess fissile materials is a titanate-based ceramic. The current plan is to fabricate this material into approximately 6.4 cm diameter disks to be placed in a container inside the DWPF glass pour canister. The pour canister itself will be placed inside another corrosion resistant container before emplacement into a geologic repository. If this barrier system were to fail, the ceramic could be exposed to repository ground waters and the potential exists for radionuclides and/or neutron absorbers to be preferentially released from the wasteform and out of the waste package. It is the purpose of this activity plan to document the work necessary to develop a mechanistically-based model that can be used to calculate the degradation rate of the ceramic waste form.

The model to be developed will be based on data from a combination of sources, including:

1. Dissolution tests of the ceramic performed as part of the Plutonium Immobilization Project (PIP);
2. Previous titanate (Synroc) dissolution tests;
3. Physical chemical theory of kinetic rate processes.

These data will be used for waste form qualification as well as model development.

The range of conditions for which the model is applicable will be limited to conditions likely to be present in the proposed Yucca Mountain High Level Waste repository. These will include temperatures of up to 250°C under unsaturated hydrologic conditions, and up to 96°C under liquid-water-saturated conditions. Vapor phase chemistries will evolve over time, but are expected to be nearly pure water vapor, with more oxygen and carbon dioxide returning at later times ppm (TSPA95, 1995). The oxygen content of the vapor phase will therefore vary from 0 to 20 Mpa (0.2 bars), and the CO₂ content from 0 to about 1000 ppm. The fluid chemistries will be complex because of interactions with other repository materials at elevated temperatures. Corrosion and oxidation of metals could generate acid and lower the pH. Interactions with concrete could increase the pH as high as 12. Interactions with the host rock at elevated temperature can raise the dissolved cation concentration to much higher levels than the ambient groundwater. Carbonate and chloride-rich brines could be generated from water dripping and evaporating on the waste package. Because all these processes may eventually modify the water composition, and in fact different waste packages may contact different types of water, we must be able to calculate ceramic corrosion rates over this wide range of chemical conditions. Also, because Yucca Mountain Project (YMP) work is on-going in the area of predicting repository water compositions, new data will likely become available during the time the ceramic model is being developed. These new data will need to be incorporated into the model development activity.

What we consider a final model will not necessarily be a complete mechanistic model that quantifies all aspects of the ceramic dissolution

process. Once rate-limiting processes are identified, we can then provide defensible predictions of long-term waste form behavior. Conservative estimates can be made in cases where known alteration rates are less than some value limited by test characteristics such as analytical detection limits. Much of the detail of the ceramic dissolution process may not be needed for performance predictions, and in fact much is removed before the abstracted model is incorporated into performance assessment models of the repository. Modeling work will be prioritized with this awareness in mind.

2. Approach

Titanates were chosen for plutonium immobilization in part because of their presumed very slow dissolution rates in aqueous solutions. The titanate structure is composed of 6-fold coordinated Ti ions surrounded by oxygens. This titanate network is particularly resistant to hydrolysis by water which gives rise to its high durability.

2.1. Crystal Chemical Effects on Durability

The minerals likely to be present in the ceramic and to contain plutonium and uranium are given in Table 1.

Table 1. Minerals containing Pu and U present in ceramic waste form.

| Mineral | Composition | |
|-------------|-----------------------------|---|
| | Normative | In Ceramic |
| Zirconolite | $\text{CaZrTi}_2\text{O}_7$ | $(\text{Ca,Gd,Pu})(\text{Hf,Pu,U})\text{Ti}_2\text{O}_7$ |
| Pyrochlore | ----- | $(\text{Ca,Gd,Pu})(\text{Hf,Pu,U,Gd})\text{Ti}_2\text{O}_7$ |
| Brannerite | UTi_2O_6 | $(\text{Hf,Pu,U})\text{Ti}_2\text{O}_6$ |

The dominant ceramic phase will be pyrochlore, with lesser amounts of zirconolite and brannerite, depending on the impurity loading. Therefore these are the three minerals for which a dissolution model is needed in order to evaluate their stability in the repository.

Pyrochlore and zirconolite have very similar structures. Both are composed of sheets of TiO_6 octahedra. Different stacking arrangements of the sheets gives rise to the various polytypes of zirconolite. Pyrochlore has the stacking arrangement that preserves open channels in the structure and allows incorporation of large ion-exchangeable cations such as Na^+ in natural pyrochlores. One of the key questions for calculating pyrochlore stability is whether or not ion exchange of Ca^{2+} takes place in our fabricated pyrochlores and if so whether this has a negative effect on durability.

The pyrochlore-zirconolite minerals have three major crystallographic sites. For the normative zirconolite (Table 1) these can be identified with the Ca, the Zr and the Ti sites. It is likely that the three sites will differ in the ease with which the cation occupying the site can be removed through hydrolysis during dissolution. The Ti sites in the oxide framework will probably be the

most resistant, because of the small size and high charge on the Ti^{+4} ion, and the Ca sites the least resistant for opposite reasons.

The relative rates of removal of ions from the three sites are important for two major reasons. The first is that one of the key concerns with the ceramic performance in the repository has to do with relative mobilities of ^{239}Pu and its decay product ^{235}U versus the neutron absorbers Hf and Gd. In order to insure that Pu does not separate and accumulate in potentially critical masses, it is desirable that the relative release rates of Pu and the two moderators be similar, if they are released at all.

The second reason has to do with rate control of the dissolution process. Selective dissolution of one ion from the mineral, Ca for example, will give rise to a surface layer enriched in the other components, Zr and Ti. With time this layer may recrystallize. The evolving layer may perform a protective barrier and inhibit further reaction, or it may tend to flake off the surface and provide no barrier for further reaction. Identification of which mechanism is controlling the reaction rate is important because they have different rate vs. time and temperature dependencies (see below).

2.2. Oxide Dissolution Kinetic Models

Over the last 20 years, there has been a great deal of work on the topic of oxide dissolution rates in water, especially aimed at the common silicate minerals. (White and Brantley, 1995). This work has resulted in the development of kinetic theory and more detailed understanding of how oxide solids in general react with water. This work provides the basis for what is discussed here.

What is important for our purpose is to identify the rate-limiting step(s) in the reaction of the oxide solid with water. What has been found for most silicates is that the rate-limiting step is a surface reaction in which the *Si-O-Si* bonds that form the framework of the mineral are broken. The alternative theory commonly proposed to explain observed dissolution rates is based on transport limited reaction in which a surface alteration layer forms at the oxide-water interface and slows further dissolution. This slowing of the rate could be due to diffusion of water, H^+ , or OH^- through the layer, or diffusion of released cations, or some charge-coupled combination of diffusion rates.

As the work on silicates proceeded, and better methods for examining the reacted oxide surface became available, rate-limiting surface reactions were found to control the overall rate under most conditions. The same rate-limiting step (surface reaction control) was also found to be the case for borosilicate waste glasses dissolving in water. However, data for titanates are incomplete and we can not yet determine which rate-limiting mechanism controls titanate reaction rates. This is a key question that must be addressed in our experimental program.

2.2.1. Surface Reaction Rate Control

The rate law commonly used to model surface-reaction-controlled rates (Aagaard and Helgeson, 1982) has the form:

$$r = Sk \prod_i a_i^{-n_i} (1 - \exp(-A / \sigma RT)) \quad (1)$$

where r is the dissolution rate in moles per unit time, S is the reactive surface area of the solid, k is the rate coefficient (a function of mineral composition and temperature) the product term, Π accounts for the catalytic or inhibitory effects of dissolved species where a_i is the activity of species in solution and n_i is the exponent which relates its concentration to reaction rate (n_i is determined from experimental results), A is the chemical affinity (degree of undersaturation) of the dissolving oxide with respect to the solution, σ is the stoichiometric number for the rate limiting reaction step, R is the gas constant and T the temperature. When applied to oxide mineral dissolution, the rate equation is generally simplified to:

$$r = Ska_{H^+}^{-n} (1 - \frac{Q}{K}) \quad (2)$$

where all catalytic/inhibitory species other than H^+ (pH) are excluded, and the degree of undersaturation is expressed in terms of Q , the activity product of dissolved species and K , the equilibrium constant for the oxide. When the solution is far from equilibrium (highly undersaturated), Q/K is small and the affinity term $(1-Q/K)$ approaches one. The exponent $-n$ in Eqn. 2 corresponds to either s or r in Fig. 2 depending on the pH.

Thus it is critical when interpreting measured mineral dissolution rates that both the reactive surface area and the saturation state of the mineral in the leachate solution are known. The saturation state is calculated from thermodynamic data (calorimetric or solubility data) for the material. These data may, however, be estimated from dissolution test results. If these data are unavailable, the dissolution rate data cannot be interpreted in terms of the rate law (Eqn. 2).

The effects of oxide surface charge and concentrations of adsorbed ionic species also affect oxide dissolution rates. The surface charge is primarily dependent on solution pH. At low pH the surface oxygens sorb H^+ from solution and become positively charged, at high pH the oxygen ions do not sorb H^+ and retain a negative charge (Fig. 1). The crossover point at which there is no net surface charge (known as the point of zero charge, PZC) varies with the type of oxide mineral, ionic strength, and composition of fluid. For TiO_2 , which based on tests to date appears to be the phase generated on the reacted ceramic surface, the PZC is around pH 10.

Surface charge is important because oxide dissolution rates generally have minima at a pH near the PZC, with dissolution rates increasing from that point in both directions (Fig. 2). The slope r (pH < PZC) shown in Fig. 2 is usually larger than slope s (pH > PZC). If dissolution rates are too low to measure near the PZC (which is likely to be the case for titanates), rates at pH

values far from the PZC can be extrapolated to the PZC with greater confidence knowing these relationships.

In addition, plots of log reaction rate vs. surface charge generally have integer slopes, whereas plots of log reaction rate vs pH have non-integer slopes (Stumm and Wieland, 1990). This suggests a fundamental role of surface charge on the dissolution mechanism and therefore provides a better mechanistic basis for any model in which surface charge is used as a primary variable.

If the titanate ceramic dissolution rate is controlled by surface reactions, we expect alteration layers, if they are present, to be in loose contact with the oxide surface. They may crack, or readily spall. They should not physically

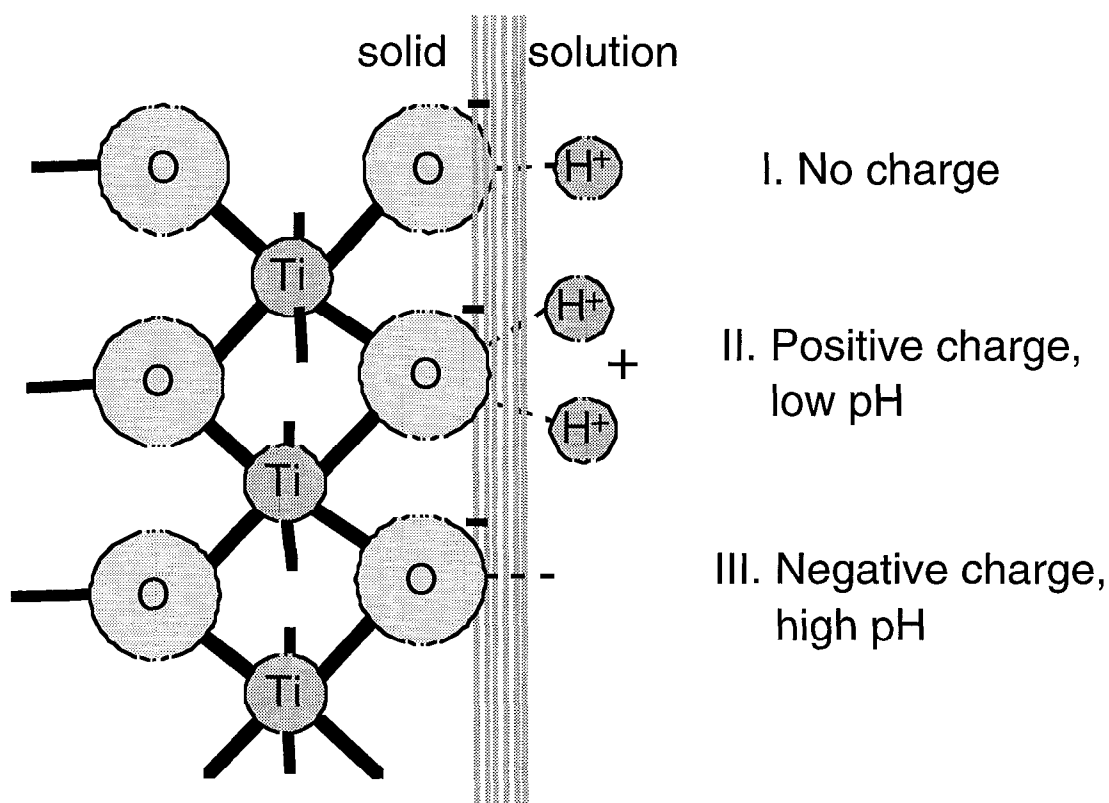


Figure 1. Surface charge characteristics of titanate-aqueous solution interface.

restrict water contact with the ceramic to the extent that it affects the reaction rate. If they did, the reaction would not be surface reaction controlled and we would see the appropriate experimental results indicating transport control.

2.2.2. Transport-Limited Rate Control

Transport-limited rate control implies that the rate which Ti-O bonds break is rapid relative to the transport of the reaction constituents to or away from the site where the reaction occurs. This could be true for a situation in which as

the ceramic reacts, a solid reaction product forms and becomes a barrier to further influx of water (or H^+ or OH^-), or slows the rate of removal of reaction

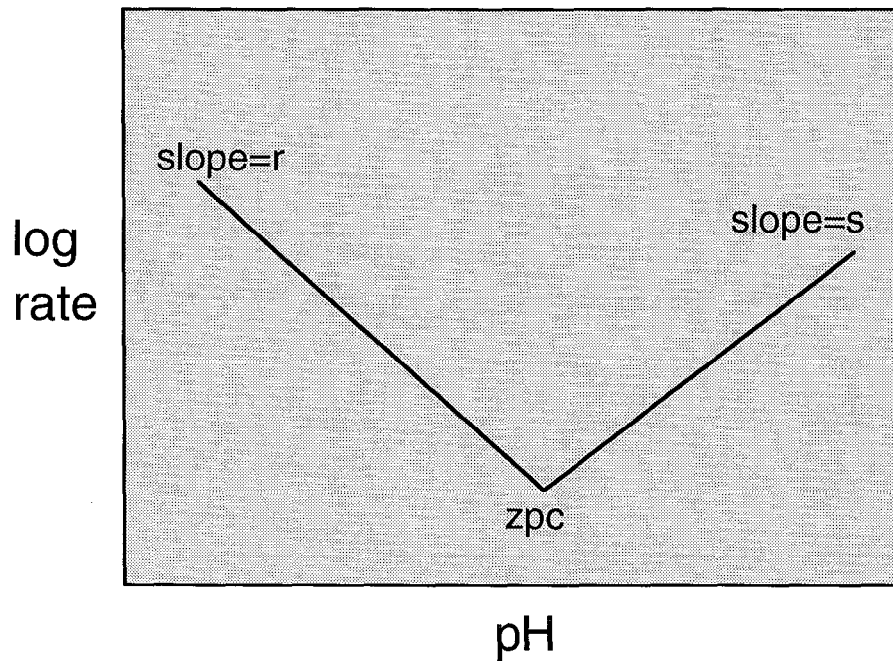


Figure 2. Schematic of relationship of dissolution rate vs pH for oxides.

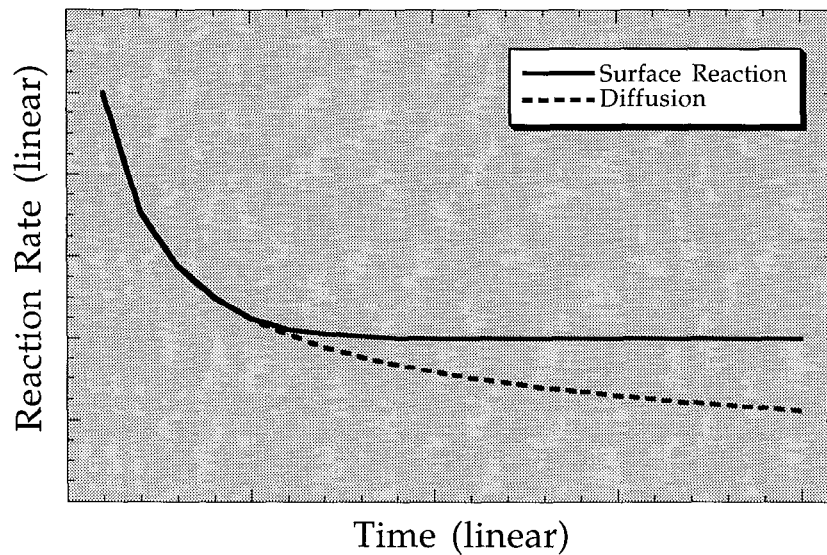


Figure 3. Characteristic results for reaction rate vs. time in flow-through tests (SPFT) for surface reaction and diffusion rate control.

products such as Ca or U*. With time, the reaction product (alteration layer) thickens and the overall reaction rate decreases accordingly. This diffusion limited process will have a rate, defined as the flux across the solution/alteration layer interface, that is proportional to $1/t^{1/2}$ (Cussler, 1984). Figure 3 shows schematically how the measured reaction rates in flow-through tests (SPFT tests, see Table 2 below) should appear as a function of time for pure surface reaction control and pure diffusive transport rate control.

For transport-rate-limited reactions, we expect to find an alteration layer in close contact and tightly adhering to the ceramic surface (see Fig. 4a). It is possible that with time, the alteration layer may age and crack, putting the ceramic back in a mode in which surface reactions control release rates.

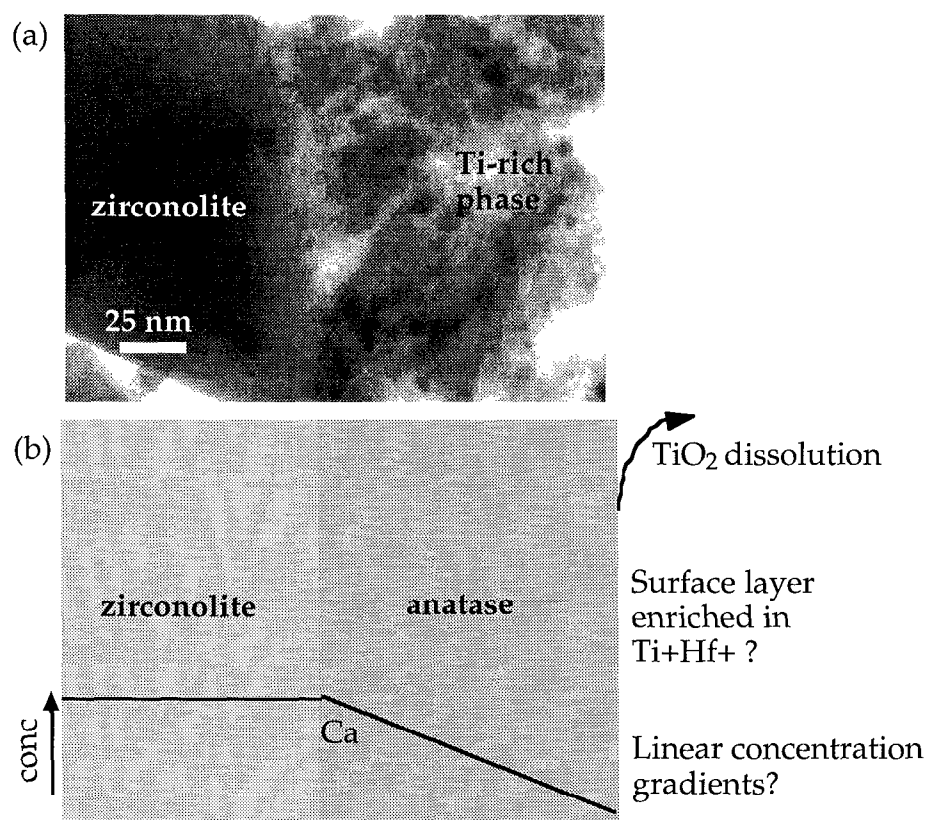


Figure 4. Reacted zirconolite: (a) TEM image of reaction surface showing ~100 nm thick Ti-rich alteration layer, which is identified as anatase (TiO₂) by electron diffraction (E. Buck, pers. com.). (b) Schematic of reacted zirconolite and hypothetical Ca concentration through alteration layer assuming steady state transport-limited dissolution.

* Rates of transport of species through the aqueous phase are known to be rapid relative to network hydrolysis reactions and not rate limiting for relatively insoluble solids such as the titanates.

Finally, it is possible that some combination of transport and surface reaction control will limit overall reaction rates. If an alteration layer forms, this alteration layer will have some finite dissolution rate. The dissolution rate of the anatase alteration layer will determine the rate at which the anatase-solution boundary moves (towards the left as shown in Fig. 4). The rate of movement of the zirconolite-anatase boundary is determined by the rate of reaction of the zirconolite with solution components, which have diffused through the anatase alteration layer. Coupling between the two processes will give rise to a steady-state condition in which the anatase alteration layer assumes a constant thickness and the reaction rate of the zirconolite is constant. The slower the rate of dissolution of the protective TiO_2 layer, the thicker the layer becomes. Anatase alteration layers have been observed on reacted zirconolite ceramics (Fig. 3 and (Lumpkin et al., 1995)), although it is not certain that the layers were continuous and provided a transport barrier for dissolution.

Some key experimental data that we need to evaluate this reaction mechanism include: (1) Measurements of ion concentrations through the alteration layers (using methods such as the ion probe, secondary ion mass spectroscopy (SIMS), Rutherford Backscattering Spectroscopy (RBS) or others). Diffusion theory predicts they should be linear at steady-state if they are diffusing through a homogeneous material; (2) The dissolution rate of anatase, or other rate-controlling alteration phase, measured in a separate experiment. A useful validation of the diffusion model is to check whether the dissolution rate of the TiO_2 protective layer determined from modeling the dissolution process is consistent with the rate from experiments.

In order to simplify the interpretation, the ceramic dissolution rate experiments should be performed on single-phase solids, and release rate data should be collected for all of the cations: Ca, Gd, U, Pu, Hf, and Ti, and include their concentration gradients through the layers and their distribution over space in the altered layer.

The effects of temperature on reaction rate differ between surface reaction and diffusive transport control. Activation energies for surface reaction control for silicates are generally in the range of 60-100 kJ/mole (Lasaga, 1990). They are high because of the high strength of the Si-O bond. Although there are few useful data available, the Ti-O bond is also strong so that similar large values for the activation energy for dissolution of titanates are expected. In contrast, the activation energies for diffusion of ions through partially hydrous porous media are expected to be much lower, in the range of 20-40 kJ/mole (Lasaga, 1981). Therefore, the rate dependence on temperature for the two processes are much different. The rate should increase much more rapidly with temperature for surface-reaction-controlled processes than for diffusion-controlled processes. Reaction rates measured at different temperatures will provide estimates for the activation energy for the reaction and should help indicate the correct rate-controlling mechanism.

Figure 5 shows schematically the possible evolution of a pyrochlore or zirconolite grain as it reacts with an aqueous solution. However, there may be other as yet unidentified mechanisms that control reaction rates of titanates with water. This must be kept in mind as the modeling work proceeds. It

should not be assumed that any of the mechanisms or interpretations described here are necessarily correct.

2.2.3. Evolution of Ceramic Surface Area

For any type of rate-limiting dissolution mechanism, there will be some dependence of reaction rate on sample reactive surface area. For both surface reaction and diffusion-limited reactions, the overall rate will be proportional to sample surface area contacted by water. In the case of a multi-phase material, the overall rate will be determined by the sum of the rates of each phase weighted by their respective surface areas. Therefore it is important to know what the reactive surface area is and how it evolves with time. It seems likely that the surface area of the ceramic will change as it alters.

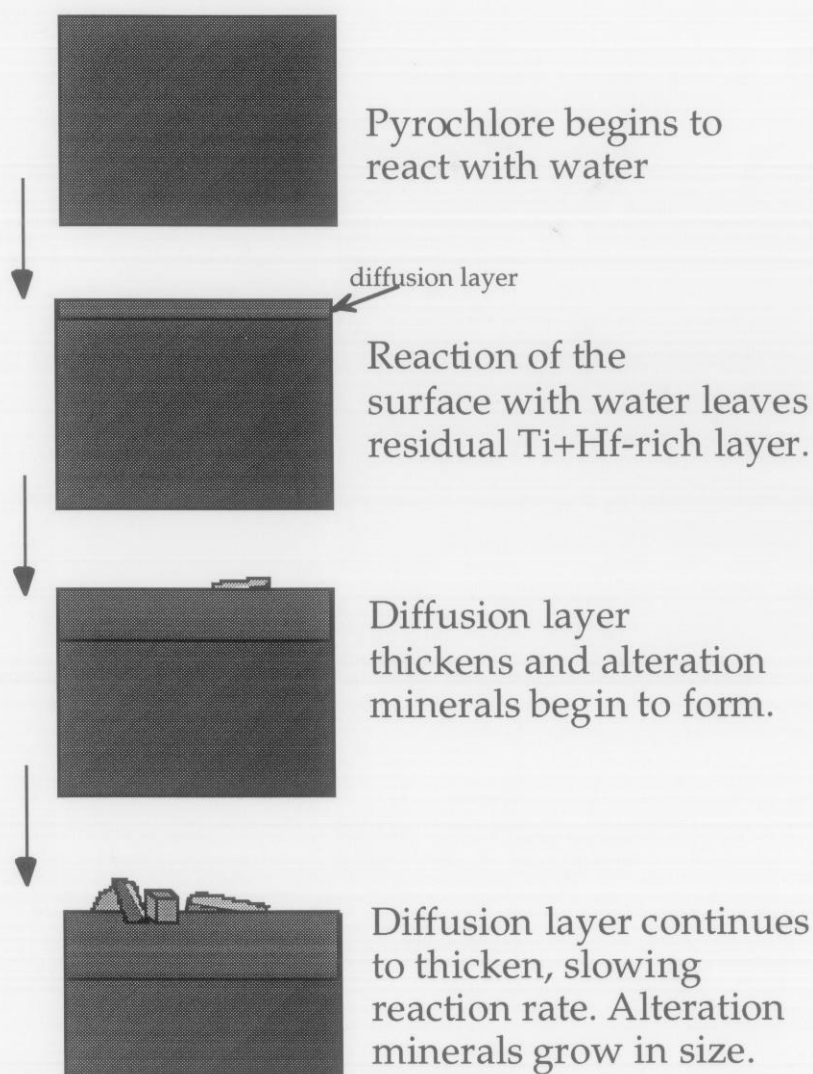


Figure 5. Possible evolution of pyrochlore reacting with water showing formation of alteration layer and alteration minerals.

Fig. 6 shows three possible paths. Previous experimental work on titanates has shown that a Ti-rich oxide layer usually forms on the reacted ceramic surface (Smith et al., 1997). If such a layer forms, it could form a barrier over the entire ceramic (Fig. 6a) or form a layer around individual grains (Fig. 6c), and perhaps only some mineral types. Alternatively, some dissolution studies of titanate ceramics indicate there is an early release pulse of some elements that may be due to selective dissolution of grain boundaries (Reeve et al., 1989) in which case the reaction may actually open up grain boundaries to further attack by water (Fig. 6b). The layer of leached grain boundaries may deepen with time as happens during dissolution of UO_2 and spent fuel. For a composite material made up of individual grains all of which contact a fluid medium, the total surface area is inversely proportional to the particle diameter at constant sample mass. If the average grain size decreases by a factor of two, the surface area increases by a factor of 2. A ceramic disk may have an effective particle size of as small as a centimeter due to cracking during fabrication, transport, and the thermal pulse during the DWPF pour. If, during selective dissolution along grain boundaries, the effective particle size decreases to ~10 microns, a typical size of individual mineral grains, the effective surface area is increased by a factor of $1\text{cm}/10\text{microns}$ or about 1000. Tests should be identified and performed that will can be used to determine whether or not selective dissolution can cause these sorts of increases in surface area.

Another important aspect of surface area of the ceramic has to do with effective surface area, which is the total surface area which actually contacts water under repository conditions. Only this fraction of total surface area can release radionuclides during reaction. The effective surface area depends on the total water content in the package, which is determined by the assumed rate of water flux into the package and the unsaturated hydraulic properties of the waste package materials. Pressurized unsaturated flow (PUF) experiments (McGrail et al., 1997) have also shown that corrosion of glass waste forms and precipitation of alteration phases changes the hydraulic properties of the materials. Similar effects are likely for the ceramic as a result of alteration phase formation and any radiation induced swelling, cracking, and disruption of grain boundary cohesion. Contact angles, water retention functions, and unsaturated hydraulic conductivity should be measured on the as-prepared ceramics and periodically on aged samples to determine if corrosion and secondary phase formation affects the hydraulic properties of the materials.

With time, alpha decay of the ^{239}Pu causes radiation damage to the ceramic. It is predicted that the ceramic will become metamict (amorphous) due to this radiation damage in a time period much less than 10,000 years, depending on the repository temperature (Van Konynenburg, 1997). The radiation-damaged ceramic is likely to be less durable than the undamaged ceramic based on previous leach testing of irradiated ceramics (Wald and Offerman, 1982; Wald and Weber, 1984). This decrease in durability may be due both to the higher energy state of the solid, which gives it a higher solubility, and also the development of increased surface area due to swelling and possible cracking along mineral grain boundaries. The limited available experimental data suggest that the durability of the radiation damaged ceramic will be 10 to 30 times less than the non-damaged ceramic. This

difference is similar to the measured difference in durabilities for silicate glasses versus their crystalline forms (i.e. albite ($\text{NaAlSi}_3\text{O}_8$) vs. albite glass, (Bourcier, 1997)).

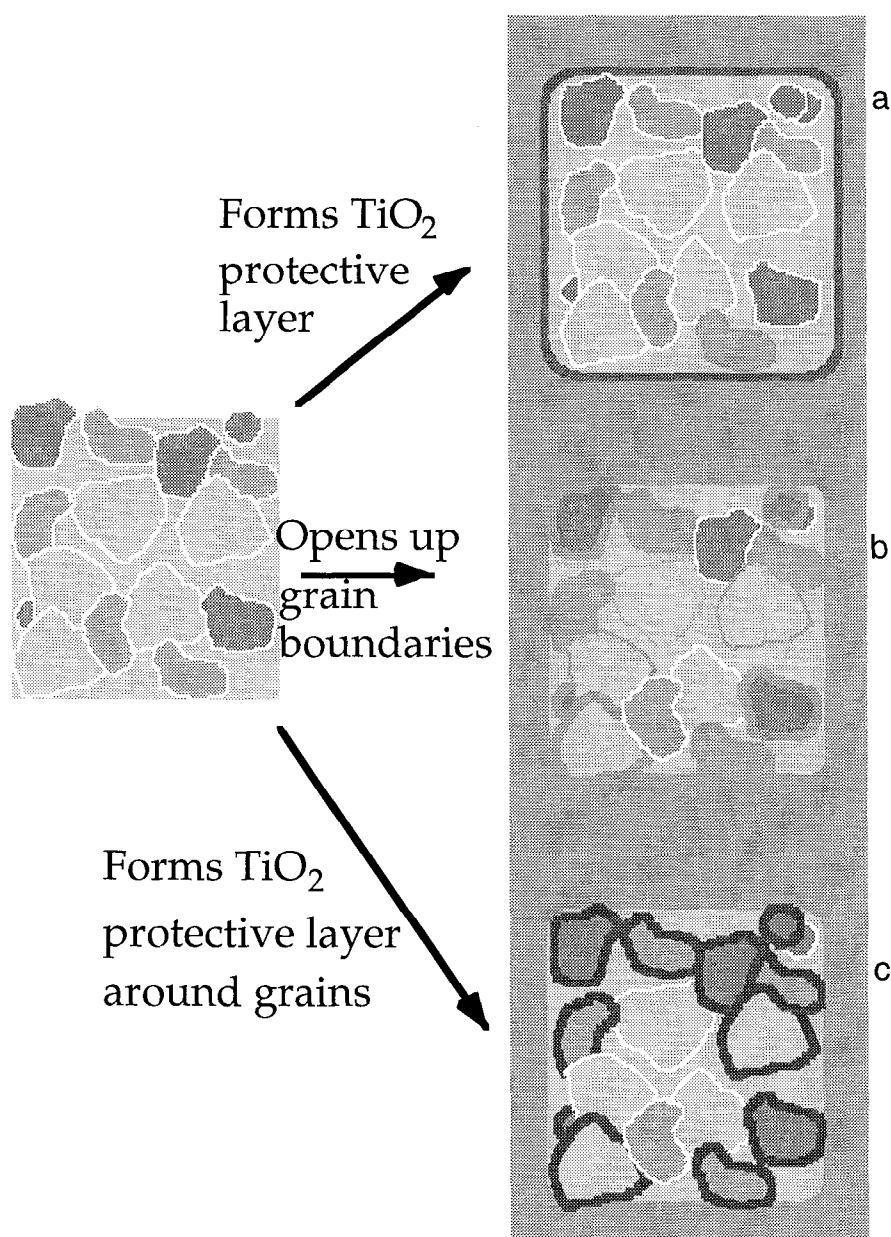


Figure 6. Possible effects of the ceramic dissolution process on surface area of ceramic-water contact.

2.2.4. The Effects of Radiation Damage

A model for ceramic dissolution clearly must account for radiation effects. Some decrease in durability is to be expected due to the radiation damage. However, over long time periods, it is possible that the Ti-rich surface layer that forms during the reaction with water will form a barrier limiting further reaction. In this case, the rate of the reaction is limited by

transport through the altered layer, and not by reactions of water with the mineral phases. If true, one would expect to see little or no difference in reaction rates between radiation-damaged and undamaged ceramics in long-term tests, defined as tests where the reaction layer has time to fully develop. Data presently available are mostly from short-term tests with durations of a few weeks or less. Long-term tests of several years duration, including tests at elevated temperatures, should help differentiate rate control and also the ultimate effects of radiation damage on ceramic alteration rates.

In addition to the radiation effect on durability, there may also be an effect due to simple transmutation. That is, what is the effect of simply changing a Pu ion to a U ion in the mineral lattice. Consequently we should do a small number of tests for U only containing ceramics for comparison with ^{238}Pu damaged samples. This effect, if present, needs to be considered in the release model.

2.3. Experiments to Support Model Development

2.3.1. Test selection

Model development is based primarily on a database of two types of experiments. The first are experiments designed to provide an understanding of the mechanisms and quantification of the rates of waste form reaction in a repository. They are performed by reacting the wasteform in systems containing repository-relevant liquids and solids under physical conditions anticipated for the repository. The second type of experiments are those designed to provide model parameters. In practice, the first type of experiment (site-specific) is initially performed in order to identify the important degradation mechanisms. Some sort of conceptual model is then formulated based on these results. Tests are then performed to provide model parameters for that model. The model is then tested (validated) with results from additional site-specific tests. This is the approach recommended in ASTM Procedure C1174-91 (ASTM, 1997) for predicting long-term behavior of materials (see Fig. 7). With this approach, results from a single experiment are not used both to determine model parameters and validate the model. To do so would be little more than a data-retrieval exercise. Instead the recommended approach uses results from a wide variety of tests to validate a model constructed from simple tests that provide the model parameters. We anticipate performing some combination of all the test types described in 2.3.2 plus other types that may be needed as the work evolves.

2.3.2. Test descriptions

Table 2 describes some of the durability tests previously used to test waste forms. It is anticipated that some combination of these types of tests and others (to be determined) will be used in this project. A brief description of each of the test types follows. A recent and more complete description of these tests is available in McGrail et al. (1998).

The MCC-1 tests are short-term (3-day) tests originally designed to screen waste forms for relative durability. Because of the low surface area of solid to solution volume ratio (S/V) for these tests, they can provide an indication of the "forward rate" of reaction, defined in terms of eqn. 2 as

conditions under which $(1-Q/K) \approx 1$. However, reaction products accumulate in solution and Q/K may differ from zero significantly. This is of concern for materials that react rapidly, but are very insoluble or form reaction products that are very insoluble.

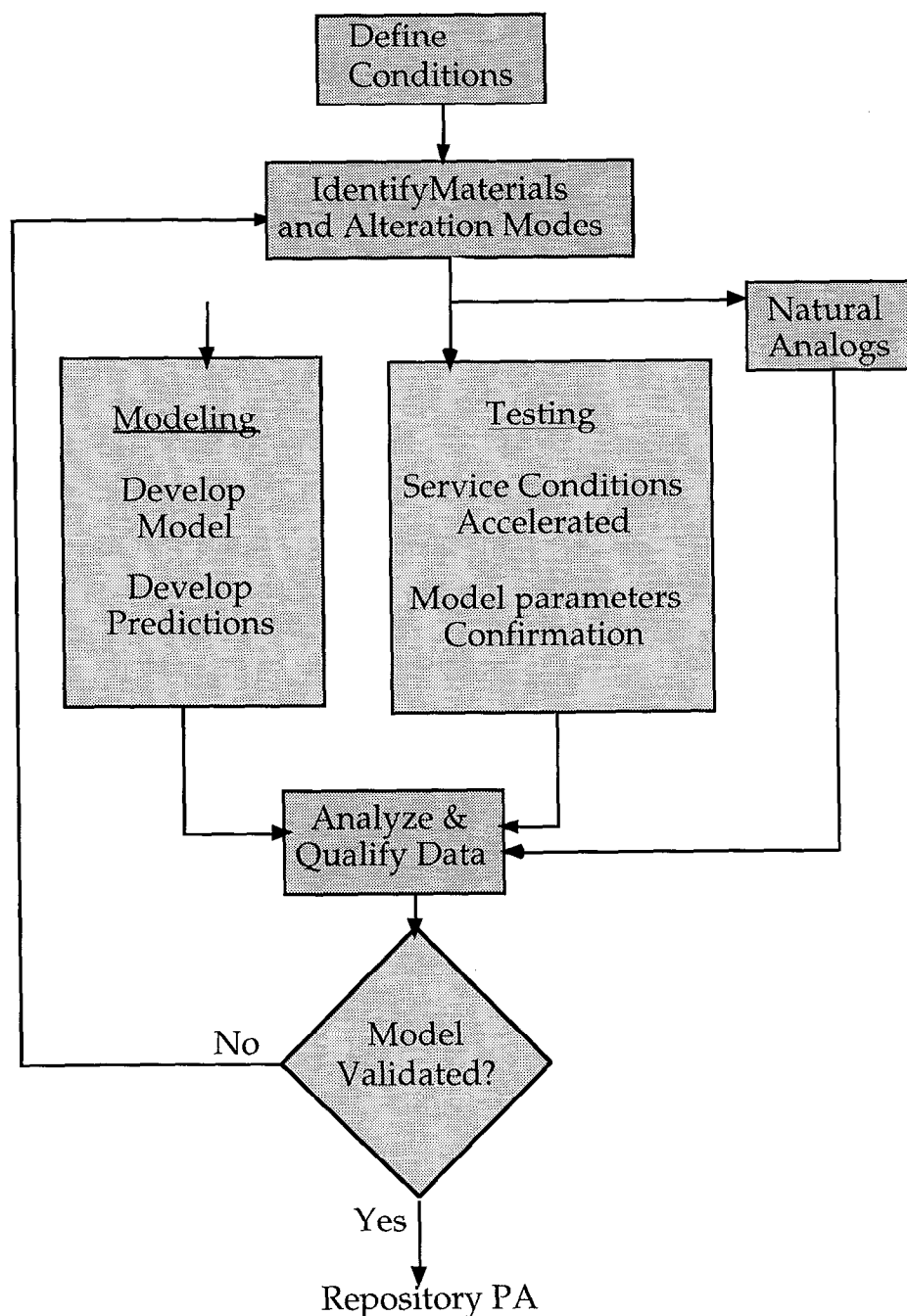


Figure 7. Simplified schematic of ASTM C1174-91 recommended procedure for predicting long-term behavior of materials in a repository.

The PCT tests use a powdered solid material so have a higher S/V than the MCC-1 test. They therefore are considered accelerated tests (see below).

The single pass flow through test (SPFT) was developed to acquire data for model parameters, in particular the value of the rate coefficient k in Eqn. 1 as a function of pH, temperature, and other solution parameters (e.g. Knauss et al., 1990). It uses a high surface area powdered solid but because the solution is constantly replenished, the reaction proceeds at the forward (far from saturation) rate, in principle.

The vapor hydration test subjects the waste form to hot humid conditions with only water vapor present, although a thin film of liquid water may be present on the ceramic surface. For a site such as Yucca Mountain which is hydrologically unsaturated, no liquid water will be present if the temperature of the repository is above the boiling point of water. This test, therefore, is used to understand waste form degradation during that time period when the repository is hot and the temperature is above boiling, and the waste form is exposed to these conditions because of container failure. Although there will be minimal transport of radionuclides away from the waste form during this time, the waste form may be significantly altered during this interval and more susceptible to later attack under saturated conditions when liquid water returns. The test uses a monolith which may be sandwiched between other repository materials such as tuff, stainless steel, or other waste forms.

Table 2. Types of waste form durability tests

| |
|--|
| <u>MCC-1</u> - One cm diameter disks polished to a 240-grit finish in a stainless steel vessel with deionized water ($S/V=10\text{m}^{-1}$) for three days at 90°C . |
| <u>Product Consistency Test (PCT)</u> - crushed material (-100+200 mesh) and deionized water in stainless steel vessels. |
| <u>PCT-A</u> - one gram of test material reacts with DI water (S/V of 1200 m^{-1}) for 7 days at 90°C . |
| <u>PCT-B</u> - five grams of test material reacts with DI water (S/V of $12,000\text{ m}^{-1}$) for various times (28-182 days) at 90°C . |
| <u>Single Pass Flow Through (SPFT)</u> - Solution of fixed composition flows through powdered sample, $25\text{-}250^{\circ}\text{C}$, reacts for days to months. |
| <u>Vapor hydration test</u> - Monolith reacted in hot humid environment. |
| <u>Unsaturated Test</u> - Drop of solution periodically drips on monolith of material. |
| <u>Pressurized Unsaturated Flow Test (PUF test)</u> - Hydraulically unsaturated flow through porous medium composed of waste form and other materials. |

The vapor hydration test also serves to accelerate the process of formation of alteration phases. It has been shown that the reaction products that form in this test are similar to those found in nature and in long-term tests with liquid water present (Ebert et al., 1991).

The unsaturated test is test in which water slowly drips onto the waste form. It is meant to simulate repository conditions in which water drips from the borehole ceiling onto the waste form to attain reactions between the waste form and water in a thin film. These reactions may be much different than

the reactions that take place in the presence of bulk water, in particular with ionizing radiation present. The test uses a monolith, which may be sandwiched between other materials.

The pressurized unsaturated flow (PUF) test is designed to simulate unsaturated hydrologic conditions with downward flow of water through a granulated ceramic material, with or without additional repository materials such as tuff, concrete and other waste forms. The test is designed to be site specific for hydrologically unsaturated conditions.

2.3.3. Accelerated Testing

Both because of the great durability of ceramic waste forms in general and the need to understand how they will perform over long time periods, it is helpful to identify experiments that potentially accelerate their reaction with water. One approach has been to scale test results of *batch tests* with a factor equal to the wasteform surface area times time divided by the solution volume ($S/V \cdot t$). This scaling principle assumes the solid slowly dissolves in water with the gradual buildup of species in solution. Various alteration minerals precipitate when they become supersaturated with respect to the solution. If $S/V \cdot t$ scaling is valid, at any point in time, the waste form reacts at a rate that is some function of the degree of its undersaturation with respect to the solution. If the surface area of the waste form is increased by a factor of two relative to the solution volume, the buildup of species in solution will be twice as fast. The system will reach the same point in "reaction progress" in half the time it would take for the smaller surface-area sample. This is one of the reasons the PCT, which uses a high surface area powdered material, is considered an accelerated test and is therefore more applicable to predicting long-term waste form behavior. This is in comparison to the MCC-1 test, which uses a relatively low surface area monolith, and results in larger forward rates which are closer in magnitude to rates measured in flow-through tests. Therefore it is believed the PCT provides information more relevant to the long-term behavior of the waste form than the MCC-1 test.

Scaling with $S/V \cdot t$ will hold for surface reaction-controlled kinetics for which there are no time-dependent nucleation and growth, nor any unaccounted ion-exchange or surface complexation reactions. The primary effect of these latter two effects is to change the pH of the solution, which can be appropriately accounted for in the analysis of the tests. For transport-limited dissolution, $S/V \cdot t$ scaling is not expected to be valid. In reality, no set of tests will follow strict $S/V \cdot t$ scaling because of kinetic processes which occur during dissolution and which do not follow $S/V \cdot t$ scaling. However, the parameter provides a useful indicator of reaction progress which helps in comparing results from different types of experiments.

Table 3 shows values of the $S/V \cdot t$ parameter for three types for the specified conditions. The PCT test has the highest value; the MCC has the lowest, and therefore may provide a useful value of the forward reaction rate provided the elemental releases are not solubility-limited.

Another way to accelerate dissolution tests is to increase temperature. However, the potential exists that the rate-limiting mechanism may change

as temperature is increased, making the high temperature rate data of limited use. This is particularly true where surface reaction and transport limited processes are involved as their activation energies are different and therefore their changes with temperature are different. As temperature is increased, it is more likely that transport-limited processes will become rate limiting because of their relatively smaller activation energies (see section 2.2.2 above).

Table 3. The S/V*t scaling factors for MCC, PCT and SPFT tests.

| | A (cm ²) | V (ml) | t (days) | S/V (cm ⁻¹) | S/V (m ⁻¹) | (S/V)*t (days/cm) |
|--------------|----------------------|--------|----------|-------------------------|------------------------|-------------------|
| SPFT* | 1000 | 4 | 0.13 | 250 | 25000 | 3250 |
| MCC-1 | 4 | 40 | 3 | 0.1 | 10 | 30 |
| PCT-A | 400 | 10 | 7 | 40 | 4000 | 28000 |

*factor for SPFT assumes 30ml/day flow rate and 4 ml cell volume

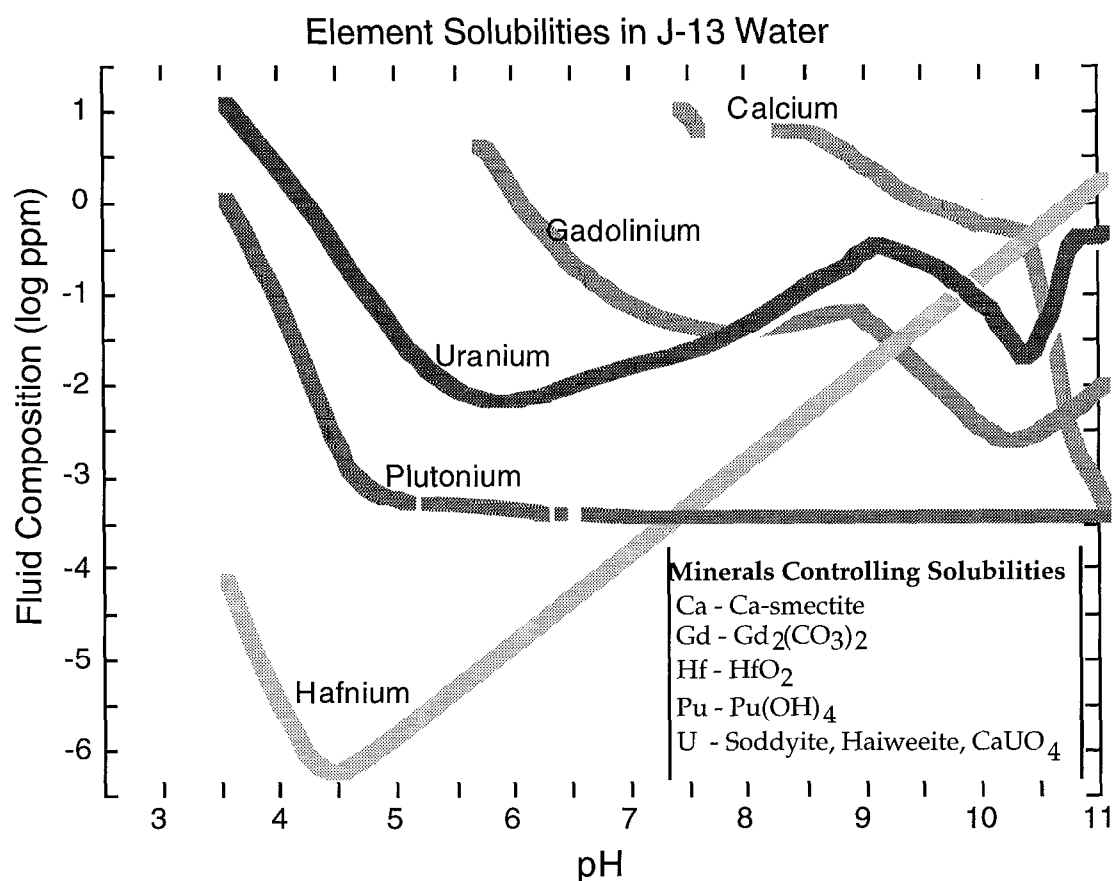
2.3.4. Solubility-Limited Release

Waste form durability tests commonly use the amounts of released elements as indicators of extent of reaction. This assumes that the element is released completely into solution and does not precipitate as an alteration phase, sorb onto the test vessel walls, or is anywhere but in solution. The ceramics we will be testing contain relatively insoluble elements. Most form very insoluble oxide or hydroxide solids, or other more complex phases when reacted in water. Figure 8 shows calculated solubilities for all of the major elements present in the ceramic. The solubilities are very low, particularly at near-neutral and alkaline pHs. Dissolution tests in which the rate of reaction causes elemental concentrations in solution to exceed solubility limits may not provide a real measure of reaction rate. Instead, the concentrations of elements in solution may instead reflect solubility limits.

Alternate methods for measuring reaction rates of the ceramic may therefore be needed in order to avoid saturation effects. One approach is to dope the ceramic with a minor amount of an element that is highly soluble in water, yet fits into the ceramic structure without greatly disrupting it. One possibility is to use an element such as molybdenum that will go into the ceramic as Mo⁺⁴ during fabrication but during dissolution in oxidizing solution will oxidize to relatively soluble MoO₄²⁻. A potential problem with molybdenum is that it does form a fairly insoluble CaMoO₄ phase. Other elements are available that may be more appropriate. Ceramics with added amounts of these elements will need to be fabricated, characterized, and tested.

An alternate method for measuring reaction rates of sparingly soluble solids with water is to use an isotope dilution method. The basis of this method is to react a solid containing an element A into a solution that has some amount of dissolved A with a different isotopic composition. As dissolution proceeds, the element released from the solid is assumed to mix isotopically with the A present in solution before precipitating in the alteration layer or as alteration minerals (Fig. 9). A small amount of dissolution can produce an easily measured change in the isotopic composition of A in solution, depending on the initial isotopic compositions

used. The method is potentially extremely sensitive. For the titanate ceramics, calcium appears to be the most appropriate element to use with this approach.



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Figure 8. Calculated solubilities of elements contained in the ceramic in ground water compositions typical of the Yucca Mountain site. The water composition is adjusted over the pH range by assuming HCl and NaOH as the acid and base added to the original pH 7.6 J-13 well water composition. Legend shows the major minerals controlling elemental solubilities. Thermodynamic data used to make this calculation are from EQ3/6 database *thermo.com.V8.R6* and are noted to be incomplete, in particular for the elements Hf and Gd.

Another test method which will be examined is the use of the atomic force microscope (AFM) combined with a flow-through reaction cell. With this technique it is possible to watch individual atomic layers dissolve from a mineral surface. From these data the dissolution rate of the mineral can be calculated. Any problems due to the effect of alteration mineral precipitation are avoided because we are not using concentrations of elements in solution to determine the reaction rate. These types of AFM reactors have been used successfully to study mineral precipitation/dissolution (Dove and Platt, 1996), recently at temperatures up to 200°C (K. Knauss, pers. com.).

No single type of test can determine the relative durabilities of two waste forms. It has been observed previously that the order of durability for

borosilicate glass waste forms can change depending upon the type of test being used. Therefore there is no single test that can be used alone as an index of ceramic durability in a repository, and there is no point in trying to identify such a test.

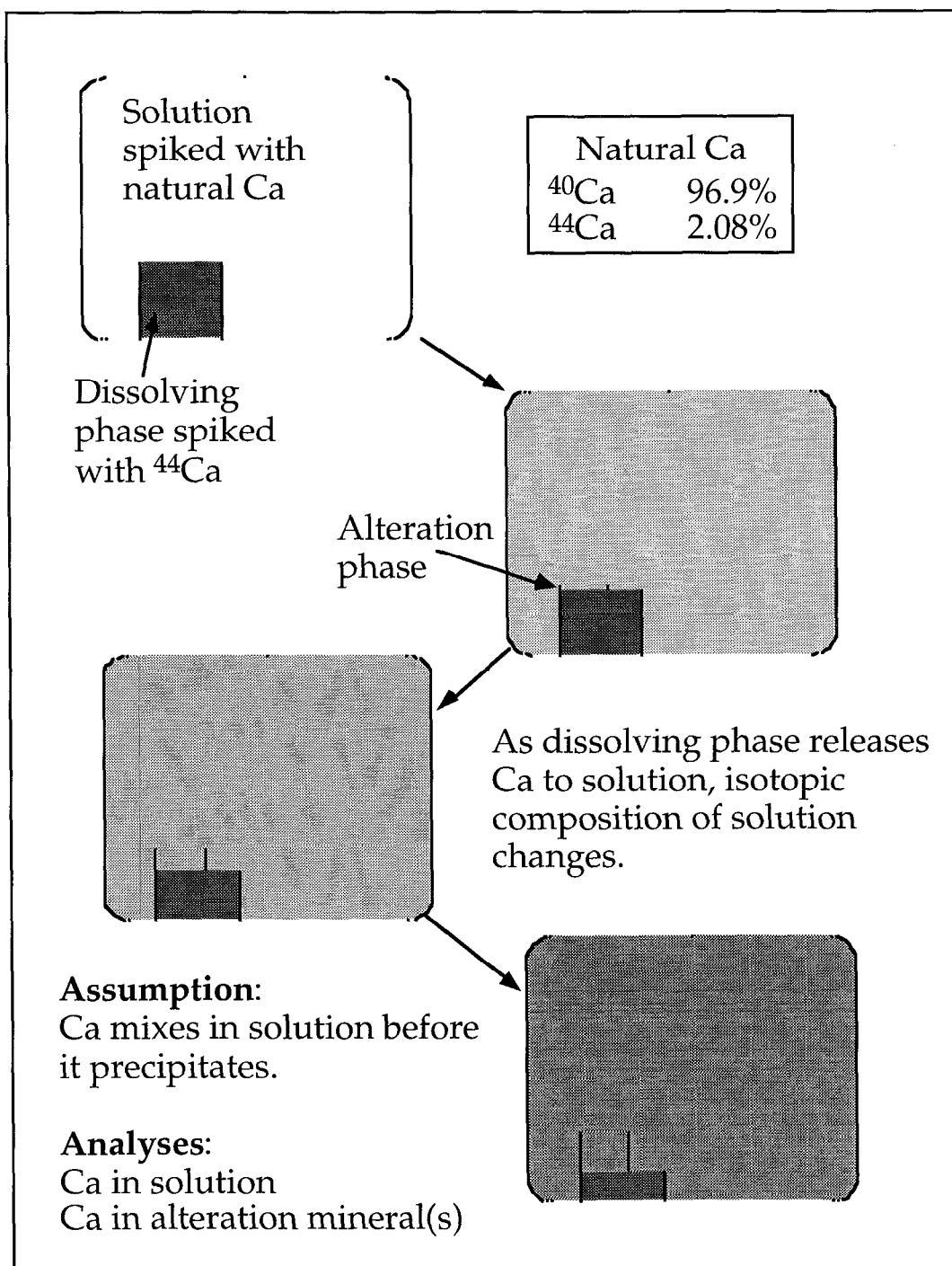


Figure 9. Schematic showing principle of isotope dilution experiment.

2.4. Model development plan

The exact sequence of activities to be performed to develop a detailed dissolution model for the ceramic will depend on experimental results. However, the approach can be described in general with the following sequence of steps:

1. Identify important chemical and physical processes taking place during dissolution process. Use experimental results from initial test matrix to determine important alteration processes and develop conceptual model(s) of dissolution process. This includes observing types of alteration layers and alteration phases that form and characterizing their properties. Do they adhere or flake off? Are there clear diffusion profiles of elements vertically through the alteration layer? Is overall dissolution stoichiometric or non-stoichiometric? How sensitive is the reaction rate to temperature? These and other questions of this nature are addressed with this work.
2. Identify rate-limiting step(s) in dissolution reaction. Use experimental results to identify or narrow possible choices of rate-limiting step(s) in the dissolution reaction. Identify the conditions over which the rate-limiting steps identified are effective i.e. over what temperature range or pH range.
3. Generate model. Use available theoretical and experimental data to generate a model. The model will be some equation or set of equations which can be used to predict the rate of ceramic degradation and release rates of radionuclides and neutron absorbers from the ceramic for a given set of environmental conditions. The mathematical model will be coupled to a geochemical modeling code in which the evolution of fluids and their interactions with other materials in the near-field environment of the repository are calculated.
4. Perform experiments that isolate processes and quantify model parameters. Carry out experiments that provide rate parameters for processes specified in 2 and conceptual model identified in 3. For example, if rates are limited by surface reactions, perform SPFT tests to determine reaction rate far from saturation as a function of pH and temperature to provide k in Eqn. 2.
5. Validate model with site-specific experimental results and natural analog studies. Test the model with data from the performance tests that were not previously used to develop or define the model. Appropriate tests may be those that test the effects of other repository materials on ceramic reaction, i.e. the PUF test, or the drip test with tuff or metals barrier materials present.
6. Develop model abstraction amenable to incorporation into the repository performance assessment model. This is a simplified version of the model that can be interfaced with the other submodels to evaluate total system performance.

2.4.1. Schedule and Milestones

We will follow the ASTM procedure to get to a viable model. This will require some iteration to refine the model and amend it as new experimental results become available. We will limit the mechanistic details of the model to the identification and quantification of the rate limiting step(s). This knowledge should allow us to calculate the effects of changes in environmental conditions on waste form behavior.

Because the process of developing a mechanistic titanate dissolution model is a scientific task and therefore a creative one, it is difficult to provide a detailed listing for what will be done at each step of the ceramic performance model development process. The design of a new experiment depends upon the outcome of the previous one, so that it is likewise impossible to provide a detailed schedule of experiments. The sequence of steps listed above are likely to be somewhat iterative, in that some false leads may be pursued, and steps 2, 3 and 4 may need to be carried out several times before the outcome is judged satisfactory. Likewise, there is no absolute method to determine whether a model is correct or not and some judgment is necessary to determine how accurate predictions need to be before the model is satisfactory for making predictions of repository performance. These questions are best answered through a peer-review process in which both outside experts and project technical personnel are involved.

The duration of this activity depends strongly on progress in the waste form testing activities. The duration of the modeling work necessary to develop an adequate ceramic dissolution model for use in licensing also depends upon the funding level. However, the overall duration of the work must include sufficient time for relatively long-term glass dissolution experiments to be completed and then used in model validation work. Experiments with durations of at least 2-3 years should be carried out to provide a minimum degree of validation of modeling results.

Milestones by year:

| | Milestones | Date |
|------|--|------|
| FY98 | Detailed model development work plan. | 4/98 |
| FY99 | Interim report on model development. | 6/99 |
| FY00 | Final report on model development. | 6/00 |
| FY01 | Report on model abstraction for performance assessment | 6/01 |
| FY02 | Update model abstraction report | 6/02 |

2.4.2. Interfaces

Interaction with other model development activities in the areas of near-field geochemistry, metal barriers, man-made materials, and hydrology are especially important for successful development of a ceramic dissolution model. These other activities define the chemical environment into which the ceramic is likely to be emplaced, and also identify the chemical perturbations to repository fluids expected during the lifetime of the

repository. All of these processes affect the composition of the fluid phase in contact with the repository. Changes in pH, oxidation state, and elemental concentrations in the fluid may affect the rates and mechanisms of corrosion of all repository materials. The coupling between all these simultaneous processes must be considered in order to predict ceramic dissolution rates accurately. The mechanistically-based ceramic dissolution model must therefore be capable of being incorporated into a performance assessment model that accounts for this coupling of simultaneously reacting repository materials. When model development is complete, the relatively complex dissolution model will need to be abstracted and simplified into a form amenable to incorporation into the repository performance assessment model (step 6 in section 2.4). This task will be done in close cooperation with technical personnel from the performance assessment technical area.

Because EQ3/6 is used in designing ceramic dissolution tests, geochemical modeling and database development also has a close interface with ceramic corrosion model development. Information exchange among the investigators of the tasks specified above and the investigators for ceramic waste form testing will be maintained on an informal basis. Information will also be obtained through review of YMP monthly reports.

Coordination must be maintained with the ceramic waste form producers. Variations in the methodology of ceramic production will influence the anticipated production ceramic compositions and therefore the ceramic compositions to be used in experiments. It will be the responsibility of the principle investigator to communicate regularly with the ceramic producers in order to maintain a current knowledge of anticipated ceramic composition and mineralogy.

In addition, mineral dissolution kinetics is currently a very active area of research in chemistry. Major breakthroughs in understanding the mechanisms of solid dissolution in aqueous solutions are anticipated in the next few years. This is due to significant improvements in surface analytical techniques, such as analytical electron microscopy (AEM), ion microprobe analysis, scanning-tunneling electron microscopy, and also in computer simulations of dissolution processes, such as molecular dynamics simulations and *ab initio* molecular orbital calculations of activated complex geometries. The knowledge obtained from this work allows development of much more refined and accurate models of actinide release from the ceramic waste form. Those changes will affect both the interpretation of our experimental work, and the types of experiments which will be performed. Incorporating this work as it comes along is important both for improving the accuracy of our calculation and also for maintaining scientific respectability of our dissolution model.

2.4.3. Work Assignments For Participating Laboratories

The model development activity will require frequent communication and close cooperation among technical personnel developing the model and those performing ceramic dissolution experiments. All of the laboratories involved in this project (ANL, ANSTO, LLNL, MIT, PNNL, WSRTC) will have a role in the model development activity. However, the primary participants in model development will be LLNL and PNNL. As more

experimental data become available, the model will become better defined in terms of alteration mechanisms and probable rate-limiting reaction steps. Feedback between model development and experimental work should continually improve the focus of the experimental program on key questions and issues related to model development. An example of this is the guidance modeling work should provide to the selection of the types of analysis to be performed on reacted samples. Are we more interested in diffusion profiles through reacted layers, or the hydraulic properties of the alteration layer, or the depth of penetration of water into the ceramic, or the solution composition of the leachate? Each of these types of data are used to constrain a different type of rate-limiting reaction. Although it would be best to obtain all of this information on each sample, time and cost will most likely not allow that. A better understanding of the reaction mechanism will lead to a better constrained and optimized experimental program needed to acquire the necessary parameters for the model, with less time and resources spent on acquiring less useful data.

3. Standards

The approach recommended in ASTM Procedure C1174-91 (ASTM, 1997) for predicting long-term behavior of materials will be followed in developing the ceramic dissolution model.

4. Technical Procedures Required

No technical implementing procedures are currently planned for this activity. The necessary information will be recorded in the scientific notebooks. No repetitive technical processes are anticipated to be part of the model development process.

5. Records

The primary documents produced as part of this activity will be scientific notebooks and computer files. Both record types will be maintained following the relevant quality assurance procedures.

6. Software

Most modeling will be performed using EQ3/6 (Wolery, 1992) and AREST-CT (Chen et al., 1996), which have been approved for quality affecting work in the Yucca Mountain Project. However, other codes may also be used. These codes will be qualified following the procedures specified in the Quality Assurance Plan. Some original modeling software, or modification of existing software may also need to be developed as part of this activity. If so, that software will be developed following the procedures specified in the Software Quality

Assurance Procedures. Other commercial software such as spreadsheets and plotting utilities will also be used. Their use will be documented in scientific notebooks and their accuracy evaluated as specified in the Quality Assurance Procedures.

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